Action Plan for Nuclear Safety - Project
Marine Monitoring: Confidence Building and Data Quality Assurance

PROGRESS REPORT

Inter-laboratory comparisons 2014-2015
Determination of radionuclides in seawater, sediment and fish

IAEA
International Atomic Energy Agency

IAEA Environment Laboratories

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SUMMARY REPORT

In the context of the IAEA Action Plan on Nuclear Safety, the IAEA, through its Environment Laboratories, is assisting the Government of Japan in ensuring that the Sea Area Monitoring Plan is comprehensive, credible and transparent. As part of the project “Marine Monitoring: Confidence Building and Data Quality Assurance”, four interlaboratory comparisons (ILCs) and two proficiency tests (PT) were organized in 2014 and 2015. The PT results published so far can be accessed on the IAEA web pages[1]. The current progress report focuses on ILCs, which are a standard means for laboratories to assess the quality of their measurement results as compared to that of other participating laboratories and identify any potentially needed improvements. Within this project, joint sampling campaigns to collect seawater (Fig A), sediment and fish samples were undertaken. The resulting samples were subsequently analysed in each participating laboratory and the results were compared.

FIG. A. Collection of seawater samples for interlaboratory comparison immediately offshore Fukushima Daiichi Nuclear Power Plant (November 2014).

In total, eight laboratories participated in at least one of the ILCs: five from Japan (participating on behalf of the Japanese authorities); the IAEA Environment Laboratories in Monaco; and, for the purpose of additional independent verification and transparency, one laboratory from Ireland and one from New Zealand, both members of the network of Analytical Laboratories for the Measurement of Environmental Radioactivity (ALMERA).

Surface seawater samples were collected during each of the four sampling missions at five sampling stations in the proximity of the Fukushima Daiichi nuclear power plant. The sampling of marine

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[1] 2014 Proficiency Test report accessible at
http://www-pub.iaea.org/MTCD/Publications/PDF/IAEA_AQ_43_web.pdf

sediment was done during a mission in May 2015 at two sampling stations in the proximity of the Fukushima Daiichi nuclear power plant. Five batches of fresh fish samples (cod, flounder and mackerel) caught at locations in the vicinity of Fukushima Daiichi Nuclear Power Plant were collected during a mission in November 2015.

Radionuclides of interest in seawater, sediment and fish were determined by participating laboratories using radioanalytical methods, including liquid scintillation counting (for ^{3}H), gas-flow proportional counting (for ^{90}Sr), alpha spectrometry (for $^{239+240}$Pu) and gamma spectrometry (for ^{134}Cs and ^{137}Cs).

The results of the laboratories were collected by the IAEA, compared and evaluated with statistical tests. For one of the exercises an independent ALMERA laboratory in Hungary (Radioanalytical Reference Laboratory of the National Food Chain Safety Office) assisted in the collection and assessment of the data. From the statistical analysis it can be concluded that the overwhelming majority of the results are not significantly different from each other (see example in Fig. B). An analysis of the whole data set demonstrated that 202 out of the 205 statistical tests applied to the data for different radionuclides and samples, i.e. over 98.5%, were passed with a high level of confidence (99%). Given that departures found are minor, i.e. for 1.5% of the statistical tests applied to the data, it can be said with confidence that the laboratories are reporting reliable and comparable results for the tested radionuclides in seawater, sediment and fish samples prepared and analysed according to each laboratory’s regularly used methods.

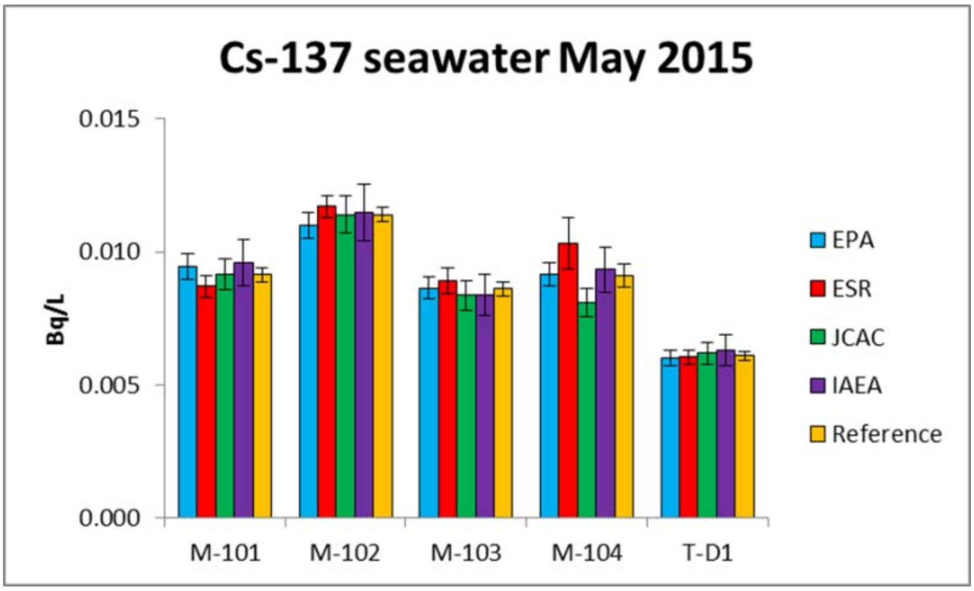

FIG. B. Example of results of an interlaboratory comparison exercise organised in May 2015: Good agreement was obtained between activity concentrations of ^{137}Cs reported by laboratories in Japan (Japan Chemical Analysis Center - JCAC), Ireland (Environmental Protection Agency – EPA), New Zealand (Institute of Environmental Science and Research – ESR) and the IAEA for each of five seawater samples (for details please refer to extended report).

Following the four sampling missions organized since mid-2014, the IAEA can confidently report that Japan's sample collection procedures follow the appropriate methodological standards required to obtain representative samples. The results obtained so far in ILCs demonstrate a high level of accuracy and competence on the part of the tested Japanese laboratories involved in the analyses of radionuclides in marine samples for the Sea Area Monitoring programme.

1. BACKGROUND

In the context of the IAEA Action Plan on Nuclear Safety, the IAEA Environment Laboratories assist the Government of Japan in ensuring that the Sea Area Monitoring Plan is comprehensive, credible and transparent. Four sampling missions were organized in 2014 and 2015 to collect seawater, sediment and fish samples for interlaboratory comparisons (ILCs). The missions were carried out within the project "Marine Monitoring: Confidence Building and Data Quality Assurance".

TABLE 1. OVERVIEW OF INTERLABORATORY COMPARISONS

Intercomparison	Seawater	Sediment	Fish	Participating laboratories
September 2014	^{3}H ^{90}Sr ^{134}Cs ^{137}Cs	–	–	GSL (^{3}H) IAEA KANSO (^{90}Sr, ^{134}Cs and ^{137}Cs)
November 2014	^{3}H ^{90}Sr ^{134}Cs ^{137}Cs	–	–	GSL (^{3}H) IAEA KANSO (^{90}Sr, ^{134}Cs and ^{137}Cs)
May 2015	^{3}H ^{90}Sr ^{134}Cs ^{137}Cs	^{134}Cs ^{137}Cs $^{239/240}$Pu	–	EPA ESR IAEA JCAC
November 2015	^{3}H ^{90}Sr ^{134}Cs ^{137}Cs	–	^{134}Cs ^{137}Cs	GSL (seawater: ^{3}H) IAEA (seawater and fish) JCAC (seawater and fish) KANSO (seawater: ^{90}Sr, ^{134}Cs and ^{137}Cs) JFFIC (fish) MERI (fish)

Participating laboratories:

EPA	Environmental Protection Agency, Ireland
ESR	Institute of Environmental Science and Research, New Zealand
GSL	Geo Science Laboratory, Japan
IAEA	IAEA Environment Laboratories, Monaco
JCAC	Japan Chemical Analysis Center, Japan
JFFIC	Japan Frozen Foods Inspection Corporation, Japan
KANSO	General Environmental Technos, Japan
MERI	Marine Ecology Research Institute, Japan

2. SEAWATER, SEDIMENT AND FISH SAMPLING AND PREPARATION

2.1. SEAWATER

Surface seawater samples were collected during all four sampling missions at five sampling stations (M-101, M-102, M-103, M-104 and T-D1) offshore Fukushima Daiichi nuclear power plant. The coordinates of the sampling stations are given in Table 2 and shown in Figure 1.

TABLE 2. COORDINATES OF THE SAMPLING STATIONS

Sampling station	Latitude (N)	Longitude (E)
M-101 (seawater)	37°25′36″	141°02′36″
M-102 (seawater)	37°25′06″	141°02′36″
M-103 (seawater)	37°26′42″	141°02′48″
M-104 (seawater)	37°24′06″	141°02′48″
T-D1 (seawater and sediment)	37°30′00″	141°04′20″
T-D9 (sediment)	37°19′23″	141°04′01″

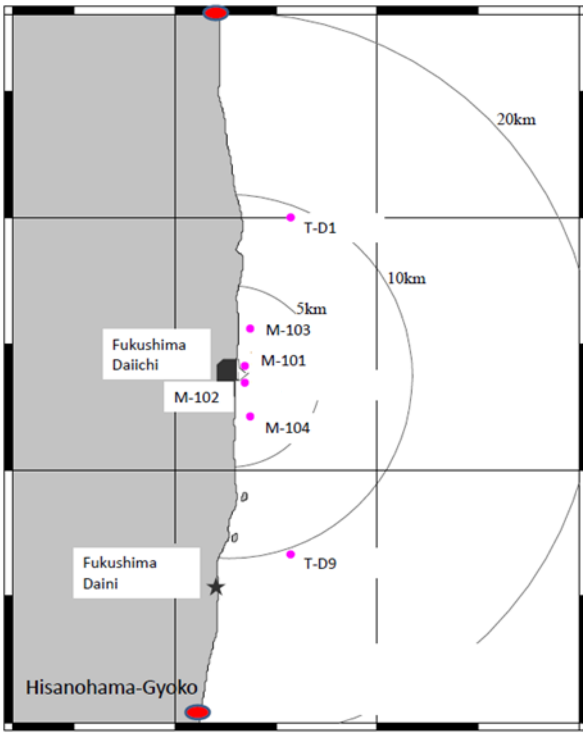

FIG. 1. Locations of sampling stations offshore Fukushima Daiichi nuclear power plant.

During the September and November 2014 missions, two surface seawater samples were collected from each sampling location for subsequent analysis for ^{90}Sr, ^{134}Cs and ^{137}Cs at a Japanese laboratory (KANSO) and the IAEA Environment laboratories in Monaco. Two separate surface seawater samples were collected at the same locations for subsequent analysis for ^{3}H at a Japanese laboratory (GSL) and the IAEA laboratories. Identical and homogeneous samples were collected using the procedures outlined below. The surface seawater was collected in Niskin bottles, mixed in a 50 L container and subsequently divided into two 20 L samples. This procedure was repeated three times at each sampling station, resulting in two 60 L of seawater samples being collected. Each sample was acidified to pH 1-2 with concentrated HNO_3. Upon arrival at the laboratory, the 60 L of seawater sample collected from each sampling station was mixed again before analysis. In the case of samples for analysis for ^{3}H, two 2 L surface seawater samples were collected for the determination of tritium at each sampling station. These samples were not acidified.

During the May and November 2015 missions, seawater samples were again collected from each sampling location for subsequent analysis for ^{90}Sr, ^{134}Cs and ^{137}Cs and, separately, for ^{3}H. As more laboratories participated in each of these exercises, a greater number of seawater samples were collected from each sampling location. In both missions, the procedure regarding the collection of 2 L seawater samples for analysis of ^{3}H was identical to the 2014 exercises described above. In the case of samples for analysis for ^{90}Sr, ^{134}Cs and ^{137}Cs, the collection and distribution method was changed however. A 400 L plastic container with four valves was first filled with seawater. 20 L containers were filled, three at a time, from each of the three/four valves (depending on the number of laboratories participating), resulting in a total of nine/twelve 20 L samples from each sampling station. Each sample was acidified to pH 1-2 with concentrated HNO_3, as for the 2014 missions. Three 20 L samples were provided to each laboratory. The seawater sampling procedure and the distribution matrix, meant to ensure the homogenisation of the samples distributed to the four laboratories participating in the May 2015 exercise, is shown in Table 3, while the distribution matrix distributed to the three laboratories participating in the November 2015 exercise is shown in Table 4.

TABLE 3. SAMPLE DISTRIBUTION BETWEEN FOUR LABORATORIES (MAY 2015)

Valve number	1	2	3	4
Seawater sample codes	1-1 1-2 1-3	2-1 2-2 2-3	3-1 3-2 3-3	4-1 4-2 4-3
Distribution pattern of the participating laboratories coded A, B, C and D	A 1-1 2-2 3-3	B 2-1 3-2 4-3	C 3-1 4-2 1-3	D 4-1 1-2 2-3

TABLE 4. SAMPLE DISTRIBUTION BETWEEN THREE LABORATORIES (NOV 2015)

Valve number	1	2	3	4
Seawater sample codes	1-1 1-2 1-3	2-1 2-2 2-3	3-1 3-2 3-3	Not used
Distribution pattern of the participating laboratories coded A, B, and C	A 1-1 2-2 3-3	B 2-1 3-2 1-3	C 3-1 1-2 2-3	–

2.2. SEDIMENT

The sampling of sediment was done during May 2015 offshore Fukushima Daiichi nuclear power plant. Sediment samples at stations T-D1 and T-D9 off Fukushima were collected using a grab sampler. The coordinates of the sampling stations are given in Table 2. The sediment samples were oven dried at 105 °C on large stainless steel trays, crushed using stainless steel spatulae and sieved through a 2-mm mesh sieve at the KANSO laboratory. No grinding was required prior to sieving due to the sandy nature of the sediments. The sieved sample was grinded using mortars and pestles, then placed in a plastic bag and mixed thoroughly to ensure homogeneity. An incremental division method was used for sample splitting. Each sample was split into two aliquots using a splitter, one aliquot was archived and the second one was further split until the required sample weight for each laboratory was attained. The sequence of splitting of each sample depended on the total weight of the sieved and grinded sample. The samples were then bottled in 500 mL plastic bottles and their homogeneity was re-checked using gamma-spectrometry. Approximately 350 g of dried sediment from each station was delivered to each participant.

2.3. FISH

Five batches of fresh fish samples (two batches of cod, two batches of flounder and one batch of mackerel) caught at locations in the vicinity of Fukushima Daiichi Nuclear Power Plant were collected from the fish landing port of Onahama on 18 November 2015 (see Table 5). The fresh fish samples were prepared the next day at the Marine Ecology Research Institute (MERI) in Onjuku (Japan) and subsequently analysed for ^{134}Cs and ^{137}Cs at MERI. After subsequent measurement on 20 November 2015 at the Japan Chemical Analysis Center (JCAC) in Chiba (Japan) and the Japan Frozen Foods Inspection Corporation (JFFIC) in Yokohama (Japan), the fresh fish samples were frozen and shipped to the IAEA Environmental Laboratories in Monaco in early January 2016. After defrosting, the fresh fish samples were measured at the IAEA Environmental Laboratories between 26 and 30 January 2016. All measurements were done by gamma spectrometry with germanium semiconductor detectors. The measurement time per sample was 1 hour for MERI, JCAC and JFFIC and between 22 and 47 hours for the IAEA. All massic activities were reported at a reference time of 18 November 2015 0:00 UTC.

TABLE 5. COORDINATES OF THE CATCH POSITION

Batch	Latitude (N)	Longitude (E)
15FA0001 cod	36°59′19″	141°28′44″
15FA0002 cod	36°59′19″	141°28′44″
15FA0003 flounder	37°06′16″	141°07′49″
15FA0004 flounder	36°54′42″	141°02′16″
15FA0005 mackerel	37°04′12″	141°16′22″

3. METHODOLOGY OF RADIONUCLIDE DETERMINATION

3.1. SEAWATER

Radionuclides of interest in seawater were determined by six laboratories participating in one or more inter-laboratory comparison: GSL, KANSO and JCAC, all participating on behalf of the Japan Nuclear Regulation Authority, and EPA, ESR and IAEA (see Table 1).

3.1.1. GSL methodology for seawater

3.1.1.1. Tritium analysis

Tritium was determined by low-background liquid scintillation counting after distillation and electrolytic enrichment.

3.1.2. KANSO methodology for seawater

3.1.2.1. ^{90}Sr analysis

KANSO used an ion exchange resin for pre-concentration of strontium from seawater sample followed by precipitation of carbonates and barium chromate. After reaching of secular equilibrium, ^{90}Y was separated using a Fe co-precipitation and measured by a gas-flow counter (Aloka LBC-472).

3.1.2.2. ^{134}Cs and ^{137}Cs analysis

Chemical separation of caesium by using AMP followed by gamma-ray spectrometry was used for ^{134}Cs and ^{137}Cs determination in seawater.

3.1.3. JCAC methodology for seawater

3.1.3.1. Tritium analysis

JCAC used liquid scintillation counter (Aloka LB-5) for measurement of tritium in seawater after distillation, electrolytic enrichment and second distillation.

3.1.3.2. ^{90}Sr analysis

For strontium determination ion exchange resins were used for pre-concentration of strontium from seawater sample followed by precipitation of carbonates and additional ion exchange for separation of calcium. ^{90}Y was removed by scavenging and measurement was done after reaching of secular equilibrium by low background beta counter (Aloka LBC-4211).

3.1.3.3. ^{134}Cs and ^{137}Cs analysis

Chemical separation of caesium by using AMP followed by gamma-ray spectrometry was used for ^{134}Cs and ^{137}Cs determination in seawater.

3.1.4. EPA methodology for seawater

3.1.4.1. ^{134}Cs and ^{137}Cs analysis

At EPA, the previously acidified seawater samples were filtered through 0.45 µm filters and caesium was extracted using Triskem AMP-PAN resin based on a method published by Pike et al. [1]. The

AMP-PAN resin, containing ^{134}Cs and ^{137}Cs, was counted by gamma ray spectrometry using a high-purity germanium (HPGe) well type detector (Canberra GCW2023).

3.1.5. ESR methodology for seawater

3.1.5.1. ^{90}Sr analysis

ESR used a method based on Eichrom Sr resin was used for the determination of ^{90}Sr in seawater.

3.1.5.2. ^{134}Cs and ^{137}Cs analysis

ESR used the Eichrom potassium nickel ferrocyanate (KNiFC-PAN) resin method for determination of ^{134}Cs and ^{137}Cs from 20 L of seawater. The resin containing caesium radioisotopes was counted by gamma spectrometry.

3.1.6. IAEA methodology for seawater

3.1.6.1. Tritium analysis

Tritium was determined by liquid scintillation counting after double vacuum distillation (at 35°C) and electrolytic enrichment followed by a second distillation (under atmospheric pressure). An ultra-low level liquid scintillation counter (Quantulus 1220) was used for the counting of an aliquot of the enriched and distilled sample mixed with Quicksafe 400 scintillation cocktail.

3.1.6.2. ^{90}Sr analysis

At the IAEA, liquid-liquid extraction with di-(2-ethylhexyl)phosphoric acid (HDEHP) was used for the separation of yttrium from seawater samples, while caesium was precipitated from the same sample by using ammonium molybdophosphate (AMP). Only for the samples from sampling stations M-101 and M-102 in the September 2014 mission, sequential separation by precipitation of MnO_2 (Pu and Am), AMP (Cs) and oxalate (Sr) was used. The ^{90}Sr activity concentration is calculated based on the measurement of ^{90}Y (yttrium oxalate source) beta activity using a proportional counter (Risø National Laboratory model GM-25-5, Roskilde, Denmark) with an efficiency of up to 44%.

3.1.6.3. ^{134}Cs and ^{137}Cs analysis

^{134}Cs and ^{137}Cs were measured by low-level HPGe gamma-ray spectrometry (EURISYS SYSTEME coaxial HPGe detector model EGC 50-200-R with 47.5 % relative efficiency). The counting time was set to obtain a counting uncertainty of less than 5%.

3.2. SEDIMENT

Radionuclides of interest in sediment samples were determined by four laboratories participating in the May 2015 inter-laboratory comparison: JCAC, participating on behalf of the Japan Nuclear Regulation Authority, and EPA, ESR and IAEA (see Table 1).

3.2.1. JCAC methodology for sediment

3.2.1.1. ^{134}Cs and ^{137}Cs analysis

JCAC used direct counting by a p-type coaxial gamma-ray detector with a relative efficiency 31% for determination of ^{134}Cs and ^{137}Cs in sediments.

3.2.1.2. $^{239+240}$Pu analysis

Plutonium radioisotopes in sediments were determined by alpha spectrometry after leaching, separation of plutonium by using of ion exchange and preparation of source by electrodeposition.

3.2.2. EPA methodology for sediment

3.2.2.1. ^{134}Cs and ^{137}Cs analysis

At EPA, ^{134}Cs and ^{137}Cs in re-homogenised and re-dried sediment samples were counted on a germanium detector (Canberra GC7520/S). Canberra ApexGamma (Genie 2k) software was used for the analysis of the obtained spectra, while coincidence summing and attenuation corrections were applied using the GESPECOR Monte-Carlo software.

3.2.2.2. $^{239+240}$Pu analysis

The method for the determination of plutonium radioisotopes used at EPA is based on work by Luisier et al. [2]. This technique utilises Triskem DGA resin in association with TEVA resin for the sequential determination of plutonium and americium radioisotopes in environmental samples. Alpha spectrometry has been used for the measurement of $^{239+240}$Pu in sediments.

3.2.3. ESR methodology for sediment

3.2.3.1. ^{134}Cs and ^{137}Cs analysis

ESR counted ^{134}Cs and ^{137}Cs in sediments in a cylinder geometry by gamma spectrometry.

3.2.3.2. $^{239+240}$Pu analysis

An Eichrom method based on using of TEVA and TRU resins followed by alpha spectrometry was used for the determination of plutonium isotopes.

3.2.4. IAEA methodology for sediment

3.2.4.1. ^{134}Cs and ^{137}Cs analysis

At the IAEA, 40 g of sediment was sealed in a tin can and ^{134}Cs and ^{137}Cs were measured by a germanium detector (EURISYS SYSTEME coaxial HPGe detector model EGPC 170-210-R) with cosmic veto shielding and relative efficiency of 170 %.

3.2.4.2. $^{239+240}$Pu analysis

The method for the determination of plutonium radioisotopes in sediments was based on classical digestion followed by ion exchange, electrodeposition and counting by alpha spectrometry. An aliquot of 5 g of sediment sample was ashed and spiked with ^{242}Pu tracer. The sample was totally dissolved by using concentrated acids. After $Fe(OH)_3$ precipitation and plutonium oxidation state adjustment, double ion exchange (DOWEX 1X4) was used for Pu purification. Plutonium was electrodeposited from Na_2SO_4/H_2SO_4 electrolyte solution on stainless steel discs and counted by alpha spectrometry.

3.3. FISH

Radionuclides of interest in fish samples were determined by four laboratories participating in the November 2015 inter-laboratory comparison: MERI, JCAC and JFFIC, all participating on behalf of the Japan Fisheries Agency, and IAEA (see Table 1).

3.3.1. MERI methodology for fish

MERI used direct counting by p-type coaxial Ge gamma-ray detectors with relative efficiencies between 28% and 46% for the determination of ^{134}Cs and ^{137}Cs in fish. The sample mass was 2 kg and each sample was measured for 1 hour.

3.3.2. JCAC methodology for fish

JCAC used direct counting by p-type coaxial Ge gamma-ray detectors with relative efficiencies between 29% and 33% for the determination of ^{134}Cs and ^{137}Cs in fish. The sample mass was 2 kg and each sample was measured for 1 hour.

3.3.3. JFFIC methodology for fish

JFFIC used direct counting by p-type coaxial Ge gamma-ray detectors with relative efficiencies between 22% and 32% for the determination of ^{134}Cs and ^{137}Cs in fish. The sample mass was 2 kg and each sample was measured for 1 hour.

3.3.4. IAEA methodology for fish

IAEA used direct counting by a coaxial Ge gamma-ray detector with relative efficiency of 48% for the determination of ^{134}Cs and ^{137}Cs in fish. The sample mass was 1 kg and the samples were measured between 22 and 47 hours.

4. RESULTS

4.1. GENERAL

4.1.1. Uncertainties

Uncertainties quoted in this report are combined standard uncertainties with a coverage factor of *k* = 1. The numerical result of a measurement is stated in the format xxx ± yyy, where the number following the symbol ± is the numerical value of the combined standard uncertainty and not a confidence interval, unless otherwise indicated (i.e. in Tables 14–16).

4.1.2. Reference time

All activity concentrations and massic activities were reported at reference times specific for each of the four sampling missions.

4.2. SEAWATER

Tables 6–9 contain the results reported by the participating laboratories for the activity concentrations of radionuclides in the seawater samples.

TABLE 6. ^{3}H ACTIVITY CONCENTRATIONS (Bq L^{-1}) IN SEAWATER

		IAEA	GSL	JCAC
Sep 2014	M-101	0.17 ± 0.04	0.171 ± 0.016	–
	M-102	0.14 ± 0.03	0.129 ± 0.015	–
	M-103	0.16 ± 0.04	0.101 ± 0.014	–
	M-104	0.15 ± 0.03	0.151 ± 0.016	–
	T-D1	0.10 ± 0.03	0.123 ± 0.015	–
Nov 2014	M-101	0.12 ± 0.04	0.175 ± 0.016	–
	M-102	0.16 ± 0.04	0.114 ± 0.013	–
	M-103	0.12 ± 0.04	0.118 ± 0.014	–
	M-104	0.14 ± 0.04	0.117 ± 0.013	–
	T-D1	0.14 ± 0.04	0.083 ± 0.013	–
May 2015	M-101	0.14 ± 0.05	–	0.08 ± 0.02
	M-102	0.08 ± 0.04	–	0.09 ± 0.02
	M-103	0.07 ± 0.03	–	0.09 ± 0.02
	M-104	0.08 ± 0.04	–	0.08 ± 0.02
	T-D1	0.06 ± 0.03	–	0.08 ± 0.02
Nov 2015	M-101	0.10 ± 0.04	0.093 ± 0.014	0.099 ± 0.021
	M-102	0.09 ± 0.04	0.109 ± 0.014	0.101 ± 0.021
	M-103	0.14 ± 0.03	0.092 ± 0.014	0.083 ± 0.020
	M-104	0.12 ± 0.03	0.110 ± 0.014	0.090 ± 0.021
	T-D1	0.08 ± 0.03	0.093 ± 0.014	0.076 ± 0.020

TABLE 7. ^{90}Sr ACTIVITY CONCENTRATIONS (Bq L^{-1}) IN SEAWATER

		IAEA	KANSO	JCAC
Sep 2014	M-101	0.026 ± 0.003	0.0190 ± 0.0011	–
	M-102	0.0110 ± 0.0014	0.0100 ± 0.00007	–
	M-103	0.00125 ± 0.00009	0.00110 ± 0.00020	–
	M-104	0.0080 ± 0.0006	0.0069 ± 0.0006	–
	T-D1	0.00101 ± 0.00008	0.00086 ± 0.00017	–
Nov 2014	M-101	0.0100 ± 0.0005	0.0087 ± 0.0007	–
	M-102	0.00377 ± 0.00020	0.0036 ± 0.0004	–
	M-103	0.00276 ± 0.00015	0.0025 ± 0.0003	–
	M-104	0.00386 ± 0.00020	0.0039 ± 0.0004	–
	T-D1	0.00098 ± 0.00006	0.00110 ± 0.00021	–
May 2015*	M-101	0.00153 ± 0.00008	–	0.00160 ± 0.00016
	M-102	0.00103 ± 0.00006	–	0.00105 ± 0.00013
	M-103	0.00129 ± 0.00007	–	0.00162 ± 0.00017
	M-104	0.00084 ± 0.00005	–	0.00109 ± 0.00014
	T-D1	0.00128 ± 0.00007	–	0.00168 ± 0.00017
Nov 2015	M-101	0.00174 ± 0.00010	0.00150 ± 0.00020	0.00177 ± 0.00017
	M-102	0.0180 ± 0.0009	0.0170 ± 0.0010	0.0174 ± 0.0009
	M-103	0.00161 ± 0.00009	0.00160 ± 0.00020	0.00134 ± 0.00015
	M-104	0.00119 ± 0.00007	0.00120 ± 0.00020	0.00112 ± 0.00014
	T-D1	0.00135 ± 0.00008	0.00110 ± 0.00020	0.00110 ± 0.00014

* additional values reported by ESR (Bq L^{-1}) were <0.015 (M-101), <0.014 (M-102), <0.033 (M-103), <0.046 (M-104) and <0.022 (T-D1)

TABLE 8. ^{134}Cs ACTIVITY CONCENTRATIONS (Bq L^{-1}) IN SEAWATER

		IAEA	KANSO	ESR	JCAC
Sep 2014	M-101	0.046 ± 0.005	0.040 ± 0.005	–	–
	M-102	0.037 ± 0.004	0.039 ± 0.005	–	–
	M-103	0.0179 ± 0.0018	0.0160 ± 0.0021	–	–
	M-104	0.035 ± 0.004	0.030 ± 0.004	–	–
	T-D1	0.0023 ± 0.0003	0.0023 ± 0.0004	–	–
Nov 2014	M-101	0.0238 ± 0.0021	0.021 ± 0.003	–	–
	M-102	0.0170 ± 0.0016	0.0150 ± 0.0020	–	–
	M-103	0.0111 ± 0.0008	0.0094 ± 0.0013	–	–
	M-104	0.0120 ± 0.0009	0.0096 ± 0.0013	–	–
	T-D1	0.0072 ± 0.0006	0.0059 ± 0.0009	–	–
May 2015	M-101	0.00227 ± 0.00023	–	0.00196 ± 0.00022	0.0025 ± 0.0003
	M-102	0.0030 ± 0.0003	–	0.00288 ± 0.00018	0.0027 ± 0.0003
	M-103	0.00195 ± 0.00019	–	0.00174 ± 0.00013	0.0022 ± 0.0003
	M-104	0.00246 ± 0.00024	–	0.0025 ± 0.0005	0.0018 ± 0.0003
	T-D1	0.00143 ± 0.00016	–	0.0013 ± 0.0004	0.0015 ± 0.0003
Nov 2015	M-101	0.0066 ± 0.0006	0.0069 ± 0.0003	–	0.0074 ± 0.0005
	M-102	0.0154 ± 0.0015	0.0140 ± 0.0006	–	0.0141 ± 0.0009
	M-103	0.0083 ± 0.0008	0.0093 ± 0.0004	–	0.0111 ± 0.0007
	M-104	0.0047 ± 0.0004	0.0051 ± 0.0003	–	0.0052 ± 0.0004
	T-D1	0.0038 ± 0.0004	0.00420 ± 0.00025	–	0.0054 ± 0.0004

TABLE 9. ^{137}Cs ACTIVITY CONCENTRATIONS (Bq L^{-1}) IN SEAWATER

		IAEA	KANSO	JCAC	EPA	ESR	Reference
Sep 2014	M-101	0.134 ± 0.013	0.120 ± 0.007	–	–	–	–
	M-102	0.113 ± 0.011	0.120 ± 0.006	–	–	–	–
	M-103	0.052 ± 0.005	0.052 ± 0.003	–	–	–	–
	M-104	0.104 ± 0.010	0.094 ± 0.005	–	–	–	–
	T-D1	0.0085 ± 0.0009	0.0070 ± 0.0005	–	–	–	–
Nov 2014	M-101	0.076 ± 0.007	0.070 ± 0.004	–	–	–	–
	M-102	0.052 ± 0.005	0.0470 ± 0.0025	–	–	–	–
	M-103	0.0357 ± 0.0025	0.0350 ± 0.0019	–	–	–	–
	M-104	0.038 ± 0.003	0.0350 ± 0.0018	–	–	–	–
	T-D1	0.0214 ± 0.0016	0.0210 ± 0.0012	–	–	–	–
May 2015	M-101	0.0096 ± 0.0009	–	0.0092 ± 0.0006	0.0095 ± 0.0005	0.0087 ± 0.0004	0.0092 ± 0.0003
	M-102	0.0115 ± 0.0011	–	0.0114 ± 0.0007	0.0110 ± 0.0005	0.0117 ± 0.0004	0.0114 ± 0.0003
	M-103	0.0084 ± 0.0008	–	0.0084 ± 0.0005	0.0086 ± 0.0004	0.0089 ± 0.0005	0.0086 ± 0.0003
	M-104	0.0093 ± 0.0009	–	0.0081 ± 0.0005	0.0092 ± 0.0004	0.0103 ± 0.0010	0.0091 ± 0.0004
	T-D1	0.0063 ± 0.0006	–	0.0062 ± 0.0004	0.0060 ± 0.0003	0.0060 ± 0.0003	0.00609 ± 0.00017
Nov 2015	M-101	0.031 ± 0.003	0.0310 ± 0.0010	0.0326 ± 0.0017	–	–	–
	M-102	0.067 ± 0.006	0.0610 ± 0.0020	0.066 ± 0.003	–	–	–
	M-103	0.041 ± 0.004	0.0410 ± 0.0013	0.0472 ± 0.0024	–	–	–
	M-104	0.0219 ± 0.0020	0.0230 ± 0.0008	0.0251 ± 0.0013	–	–	–
	T-D1	0.0187 ± 0.0017	0.0190 ± 0.0007	0.0240 ± 0.0013	–	–	–

4.3. SEDIMENT

Table 10 contains the results reported by the four participating laboratories (EPA, ESR, IAEA and JCAC) for the massic activities of radionuclides in the sediment samples.

TABLE 10. RADIONUCLIDE MASSIC ACTIVITIES (Bq kg^{-1}) IN SEDIMENT

		IAEA	EPA	JCAC	ESR	Reference
^{134}Cs	T-D1	5.0 ± 0.3	5.20 ± 0.25	6.5 ± 0.5	6.6 ± 0.4	5.8 ± 0.4
	T-D9	7.15 ± 0.20	7.6 ± 0.4	7.1 ± 0.6	6.6 ± 0.3	7.12 ± 0.20
^{137}Cs	T-D1	18.3 ± 1.0	18.9 ± 0.7	27.6 ± 1.6	23.7 ± 1.0	22.0 ± 2.2
	T-D9	25.4 ± 0.5	26.8 ± 0.9	28.0 ± 1.6	23.6 ± 0.9	25.8 ± 0.9
$^{239+240}$Pu	T-D1	0.232 ± 0.012	0.32 ± 0.04	0.283 ± 0.016	0.5 ± 0.4	0.27 ± 0.03
	T-D9	0.503 ± 0.022	0.54 ± 0.09	0.490 ± 0.022	0.4 ± 0.4	0.499 ± 0.019

4.4. FISH

Tables 11 and 12 contain the results reported by the four participating laboratories (JFFIC, JCAC, MERI and IAEA) for the massic activities of radionuclides in the fish samples.

TABLE 11. Cs-134 MASSIC ACTIVITIES (Bq kg^{-1}) IN FISH

	IAEA	JFFIC	JCAC	MERI	Reference
15FA0001 cod	0.29 ± 0.03	0.27 ± 0.08	0.27 ± 0.15	0.40 ± 0.11	0.30 ± 0.03
15FA0002 cod	0.36 ± 0.03	< 0.6	< 0.6	0.31 ± 0.07	–
15FA0003 flounder	0.76 ± 0.04	0.74 ± 0.16	1.00 ± 0.21	0.88 ± 0.15	0.79 ± 0.05
15FA0004 flounder	0.74 ± 0.03	0.88 ± 0.15	1.02 ± 0.22	0.83 ± 0.11	0.79 ± 0.04
15FA0005 mackerel	0.108 ± 0.017	0.19 ± 0.13	< 0.5	0.16 ± 0.06	–

TABLE 12. Cs-137 MASSIC ACTIVITIES (Bq kg^{-1}) IN FISH

	IAEA	JFFIC	JCAC	MERI	Reference
15FA0001 cod	1.18 ± 0.04	1.14 ± 0.19	1.45 ± 0.22	1.26 ± 0.20	1.20 ± 0.05
15FA0002 cod	1.51 ± 0.04	1.88 ± 0.25	1.00 ± 0.21	1.39 ± 0.15	1.44 ± 0.17
15FA0003 flounder	3.50 ± 0.07	3.6 ± 0.3	3.6 ± 0.3	3.9 ± 0.3	3.56 ± 0.08
15FA0004 flounder	3.39 ± 0.07	4.1 ± 0.3	3.4 ± 0.3	3.58 ± 0.25	3.57 ± 0.15
15FA0005 mackerel	0.585 ± 0.022	0.59 ± 0.13	0.68 ± 0.17	0.49 ± 0.10	0.58 ± 0.03

5. STATISTICAL EVALUATION OF THE RESULTS

For the May 2015 mission (seawater and sediment), the collection of the data was carried out by the Radioanalytical Reference Laboratory of the National Food Chain Safety Office, Hungary, while the data evaluation was done by the IAEA. For all other missions, the data was collected and evaluated by the IAEA.

The statistical evaluation method used for the results depended on the size of the data set. If two or three results were received, one or three zeta tests [3] were performed.

The zeta test was defined as:

$$\zeta_{i,j} = \left| \frac{x_i - x_j}{\sqrt{u_i^2 + u_j^2}} \right| \tag{1}$$

where:

x_i is the value of laboratory i [Bq L^{-1}]
x_j is the value of laboratory j [Bq L^{-1}]
u_i is the standard uncertainty (at $k = 1$) for the value of laboratory i [Bq L^{-1}]
u_j is the standard uncertainty (at $k = 1$) for the value of laboratory j [Bq L^{-1}]

If two results were received, $\zeta_{1,2}$ was calculated, while for three received results $\zeta_{1,2}$, $\zeta_{1,3}$ and $\zeta_{2,3}$ were calculated.

If the value of the zeta test exceeded 2.58, the results were evaluated as being significantly different (at a 99% confidence level).

If the data set contained four results, the statistical evaluation consisted of a method for calculating comparison reference values [4], which is currently being used by the Consultative Committee for Ionizing Radiation, Section II: Measurement of radionuclides, CCRI(II). After calculating a reference value, a relative degree of equivalence (DoE) was calculated for each submitted result and if this relative DoE was significantly different from zero, the corresponding result was evaluated as being discrepant. The relative DoE (%) was calculated according to:

$$\text{DoE (\%)} = \frac{x_{\text{lab}} - X_{\text{ref}}}{X_{\text{ref}}} 100 \tag{2}$$

where: x_{lab} is the individual laboratory result
X_{ref} is the reference value calculated as the power-moderated mean of the combined results

The standard uncertainty of the relative DoE, u_{DoE}, was calculated according to reference [4]. If the absolute value of the relative DoE exceeded 2.58 times u_{DoE}, the corresponding result was evaluated as being discrepant (at a 99% confidence level), as the relative DoE in this case would be significantly different from zero.

5.1. SEAWATER

Table 13 contains the zeta scores for the activity concentrations of radionuclides in the seawater samples.

TABLE 13. RADIONUCLIDES IN SEAWATER; ZETA SCORES

		Sep 2014	Nov 2014	May 2015	Nov 2015
^{3}H	M-101	0.02	1.29	1.17	0.17 / 0.03 / 0.22
	M-102	0.28	1.17	0.32	0.45 / 0.24 / 0.32
	M-103	1.34	0.03	0.39	1.45 / 1.59 / 0.38
	M-104	0.10	0.48	0.10	0.30 / 0.82 / 0.79
	T-D1	0.61	1.29	0.55	0.39 / 0.12 / 0.71
^{90}Sr	M-101	1.97	1.59	0.40	1.07 / 0.17 / 1.03
	M-102	0.66	0.38	0.17	0.70 / 0.44 / 0.30
	M-103	0.70	0.70	1.81	0.06 / 1.57 / 1.04
	M-104	1.39	0.09	1.68	0.04 / 0.46 / 0.33
	T-D1	0.82	0.55	2.16	1.15 / 1.55 / 0.00
^{134}Cs	M-101	0.86	0.82	0.98 / 0.57 / 1.39	0.44 / 1.00 / 0.80
	M-102	0.36	0.78	0.35 / 0.61 / 0.40	0.88 / 0.75 / 0.10
	M-103	0.67	1.10	0.89 / 0.68 / 1.38	1.09 / **2.61** / 2.26
	M-104	0.87	1.51	0.05 / 1.71 / 1.17	0.83 / 0.77 / 0.10
	T-D1	0.08	1.25	0.25 / 0.33 / 0.44	0.77 / **2.60** / 2.33
^{137}Cs	M-101	0.91	0.75	*	0.00 / 0.46 / 0.81
	M-102	0.51	1.03	*	0.95 / 0.20 / 1.19
	M-103	0.04	0.23	*	0.00 / 1.33 / 2.27
	M-104	0.84	0.91	*	0.51 / 1.34 / 1.39
	T-D1	1.55	0.21	*	0.16 / 2.48 / **3.43**

NOTE: Format "x.xx" refers to $\zeta_{1,2}$; format "x.xx / y.yy / z.zz" refers to $\zeta_{1,2}$, $\zeta_{1,3}$ and $\zeta_{2,3}$.
* see Table 14

Table 14 contains the degrees of relative equivalence for the activity concentrations of ^{137}Cs in the seawater samples in the May 2015 mission.

TABLE 14. RADIONUCLIDES IN SEAWATER; RELATIVE DEGREE OF EQUIVALENCE (%)

		IAEA	EPA	JCAC	ESR
^{137}Cs May 2015	M-101	5 ± 23	3 ± 11	0 ± 14	–5 ± 10
	M-102	1 ± 22	–4 ± 10	0 ± 14	3 ± 8
	M-103	–2 ± 21	0 ± 10	–3 ± 14	4 ± 13
	M-104	3 ± 23	1 ± 14	–11 ± 16	13 ± 25
	T-D1	3 ± 22	–2 ± 11	2 ± 16	–1 ± 9

NOTE: The numerical results in this Table are stated in the format xx ± yy, where the number following the symbol ± is the 99% confidence interval.

5.2. SEDIMENT

Table 15 contains the degrees of relative equivalence for the massic activities of the radionuclides in the sediment samples.

TABLE 15. RADIONUCLIDES IN SEDIMENT; RELATIVE DEGREE OF EQUIVALENCE (%)

		IAEA	EPA	JCAC	ESR
^{134}Cs	T-D1	–13 ± 21	–10 ± 20	12 ± 26	14 ± 22
	T-D9	0 ± 8	7 ± 12	0 ± 20	–7 ± 11
^{137}Cs	T-D1	–17 ± 27	–14 ± 26	25 ± 29	7 ± 27
	T-D9	–2 ± 10	4 ± 11	9 ± 16	–9 ± 11
$^{239+240}$Pu	T-D1	–15 ± 30	15 ± 39	3 ± 31	82 ± 353
	T-D9	1 ± 11	7 ± 43	–2 ± 11	–14 ± 215

NOTE: The numerical results in this Table are stated in the format xx ± yy, where the number following the symbol ± is the 99% confidence interval.

5.3. FISH

Table 16 contains the degrees of relative equivalence for the massic activities of the radionuclides in the fish samples.

TABLE 16. RADIONUCLIDES IN FISH; RELATIVE DEGREE OF EQUIVALENCE (%)

		IAEA	JFFIC	JCAC	MERI
^{134}Cs	15FA0001 cod	–3 ± 22	–10 ± 65	–8 ± 122	35 ± 84
	15FA0002 cod	*	$	$	*
	15FA0003 flounder	–4 ± 13	–7 ± 49	26 ± 63	12 ± 45
	15FA0004 flounder	–6 ± 13	11 ± 45	30 ± 68	6 ± 33
	15FA0005 mackerel	#	#	$	#
^{137}Cs	15FA0001 cod	–2 ± 10	–5 ± 38	20 ± 45	5 ± 39
	15FA0002 cod	5 ± 31	31 ± 45	–31 ± 42	–3 ± 36
	15FA0003 flounder	–2 ± 5	1 ± 22	2 ± 23	9 ± 22
	15FA0004 flounder	–5 ± 11	14 ± 20	–4 ± 23	0 ± 17
	15FA0005 mackerel	1 ± 12	2 ± 56	17 ± 73	–15 ± 40

NOTE: The numerical results in this Table are stated in the format xx ± yy, where the number following the symbol ± is the 99% confidence interval.

* Value of 0.71 for $\zeta_{1,4}$

\# Values of 0.61, 0.82 and 0.23 for $\zeta_{1,2}$, $\zeta_{1,4}$ and $\zeta_{2,4}$, respectively

$ As a value less than the detection limit was submitted, no evaluation was performed

6. CONCLUSION

A detailed data analysis was performed on activity concentrations reported for ^{3}H, ^{90}Sr, ^{134}Cs and ^{137}Cs in twenty seawater samples, massic activities reported for ^{134}Cs, ^{137}Cs and $^{239+240}$Pu in two sediment samples and massic activities reported for ^{134}Cs and ^{137}Cs in five fish samples, all collected offshore Fukushima Daiichi nuclear power plant between September 2014 and November 2015. The samples were shared between the eight laboratories [EPA (Ireland), ESR (New Zealand), GSL (Japan), IAEA (Monaco), JCAC (Japan), JFFIC (Japan), KANSO (Japan) and MERI (Japan)]. From this analysis it can be concluded that the overwhelming majority of the results are not significantly different from each other. A global analysis of the whole data set demonstrated that 202 out of the 205 statistical tests applied to the data, i.e. over 98.5%, were passed with a high level of confidence (99%). The only exceptions were two zeta scores that were just marginally higher than the critical limit of 2.58 (ζ = 2.61 for ^{134}Cs in seawater sample M-103 in Nov 2015 between IAEA and JCAC; ζ = 2.60 for ^{134}Cs in seawater sample T-D1 in Nov 2015 between IAEA and JCAC) and one zeta score that was clearly higher than the critical value (ζ = 3.43 for ^{137}Cs in seawater sample T-D1 in Nov 2015 between KANSO and JCAC). Despite these minor departures, it can be said with confidence that the laboratories are reporting reliable and comparable results for the tested radionuclides in seawater, sediment and fish samples prepared and analysed according to each laboratory’s regularly used methods.

Following the four sampling missions organized since mid-2014, the IAEA can confidently report that Japan's sample collection procedures follow the appropriate methodological standards required to obtain representative samples. The results obtained so far in ILCs demonstrate a high level of accuracy and competence on the part of the tested Japanese laboratories involved in the analyses of radionuclides in marine samples for the Sea Area Monitoring programme.

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[3] INTERNAL ORGANIZATION FOR STANDARDIZATION, Statistical methods for use in proficiency testing by interlaboratory comparisons, ISO 13528:2005, Geneva (2005).

[4] POMMÉ, S., KEIGHTLEY, J., Determination of a reference value and its uncertainty through a power-moderated mean, Metrologia **52** (2015) S200.

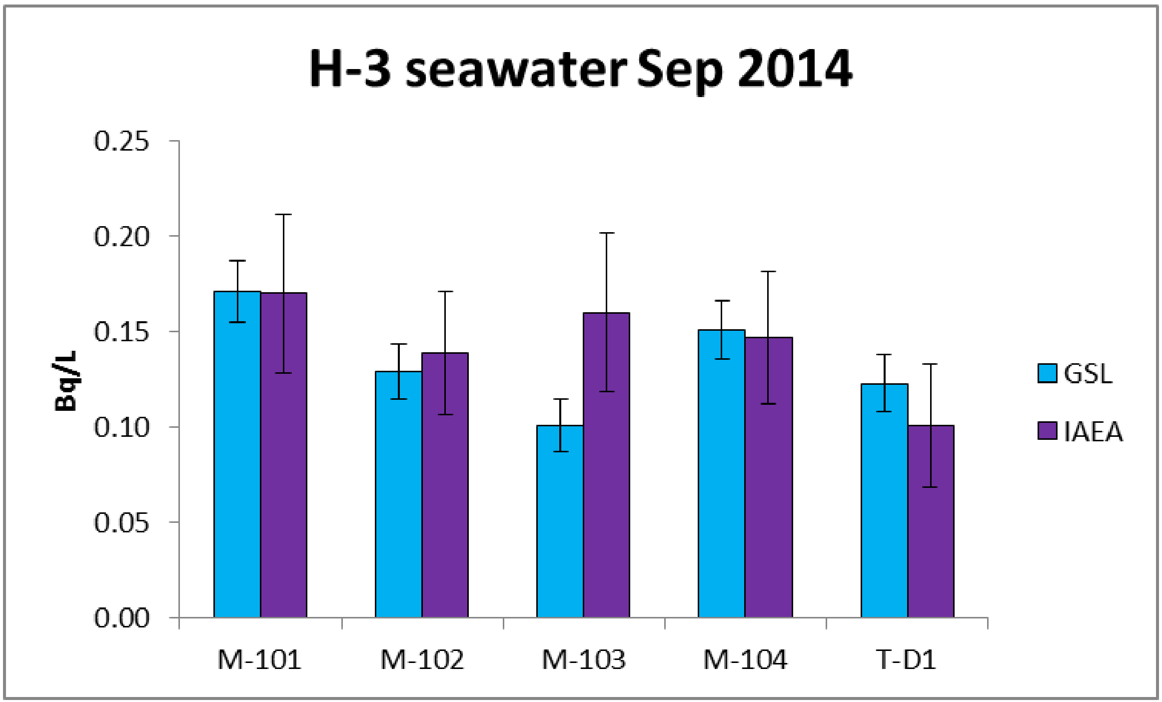

FIG. 2. Activity concentrations of ^{3}*H in seawater samples.*

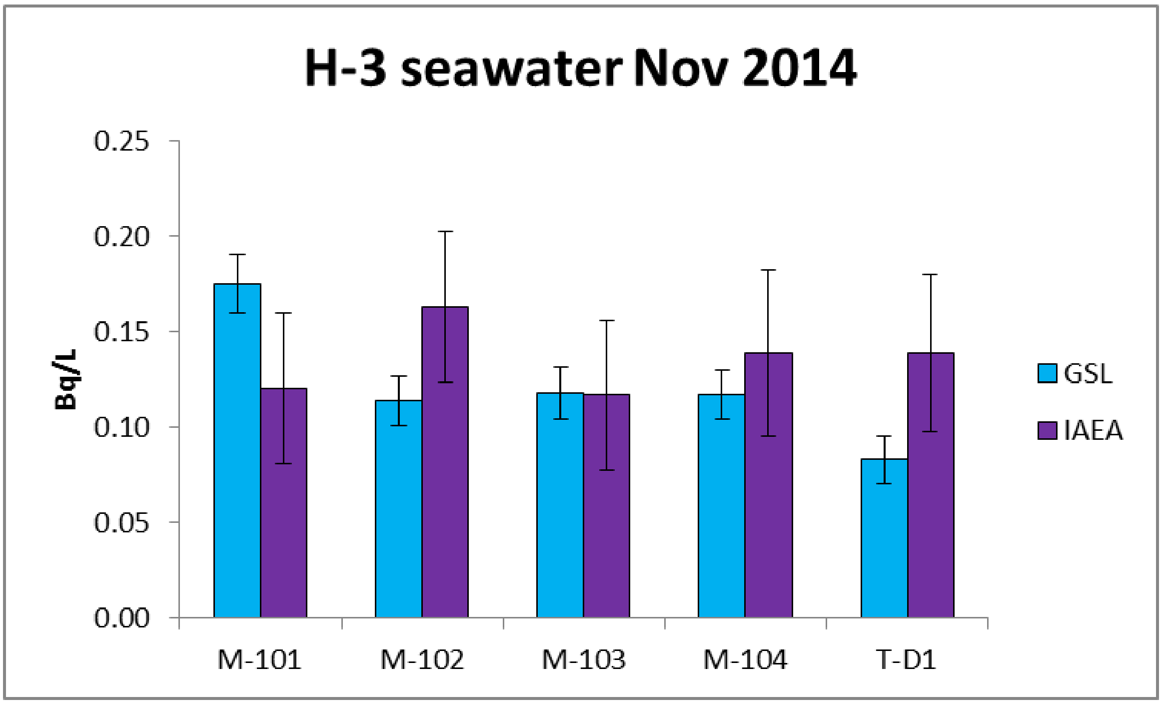

FIG. 3. Activity concentrations of ^{3}*H in seawater samples.*

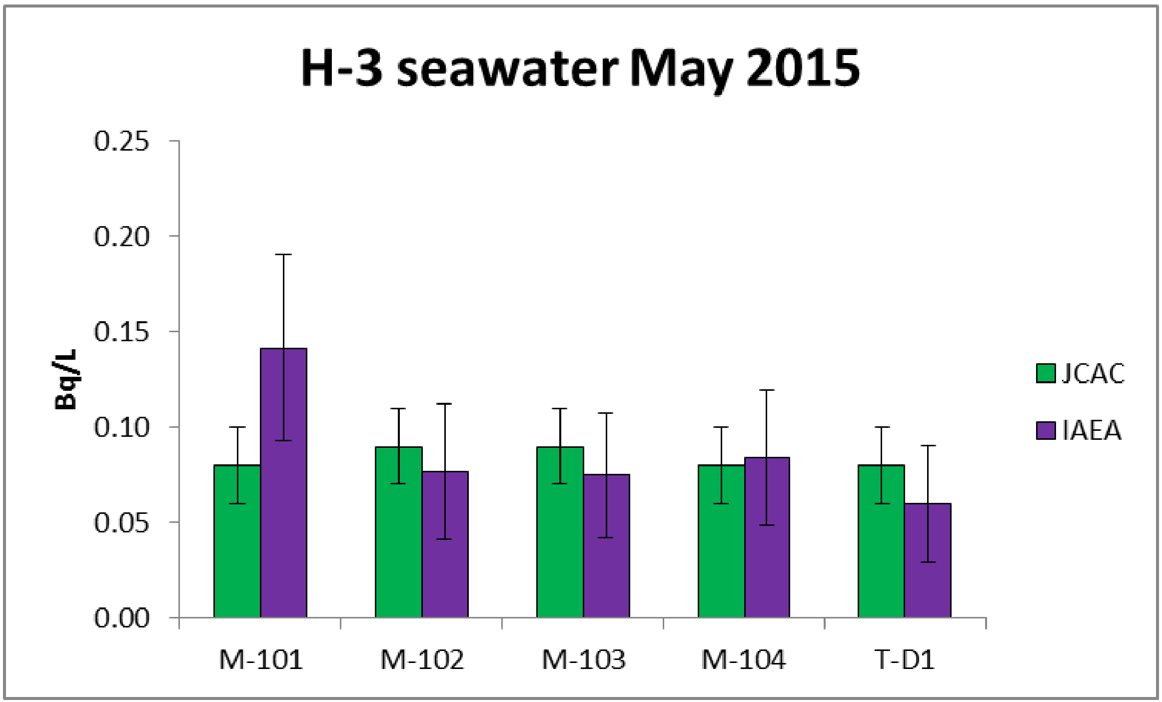

FIG. 4. Activity concentrations of ^{3}H in seawater samples.

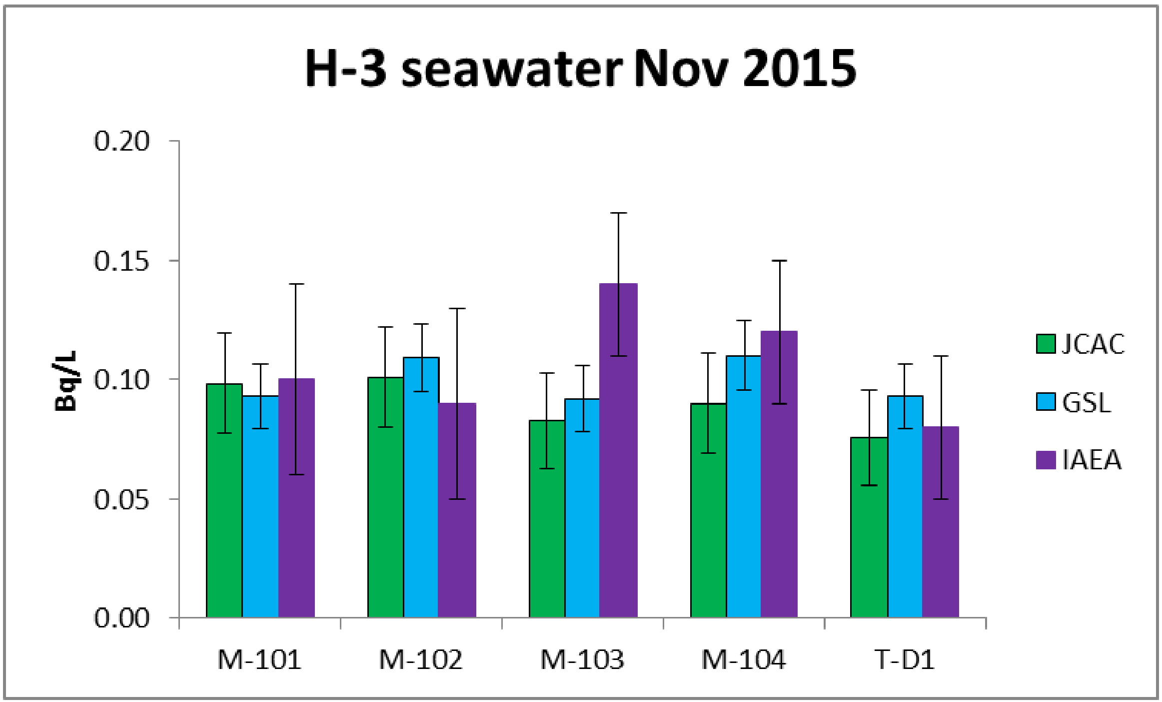

FIG. 5. Activity concentrations of ^{3}H in seawater samples.

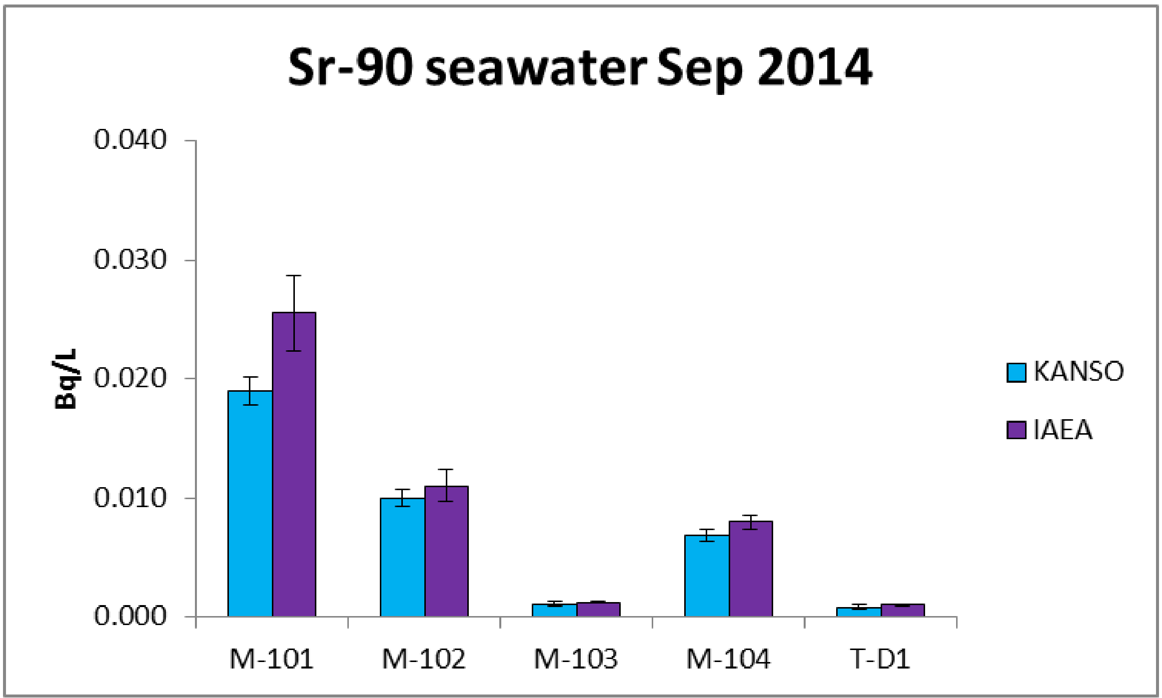

FIG. 6. Activity concentrations of ^{90}*Sr in seawater samples.*

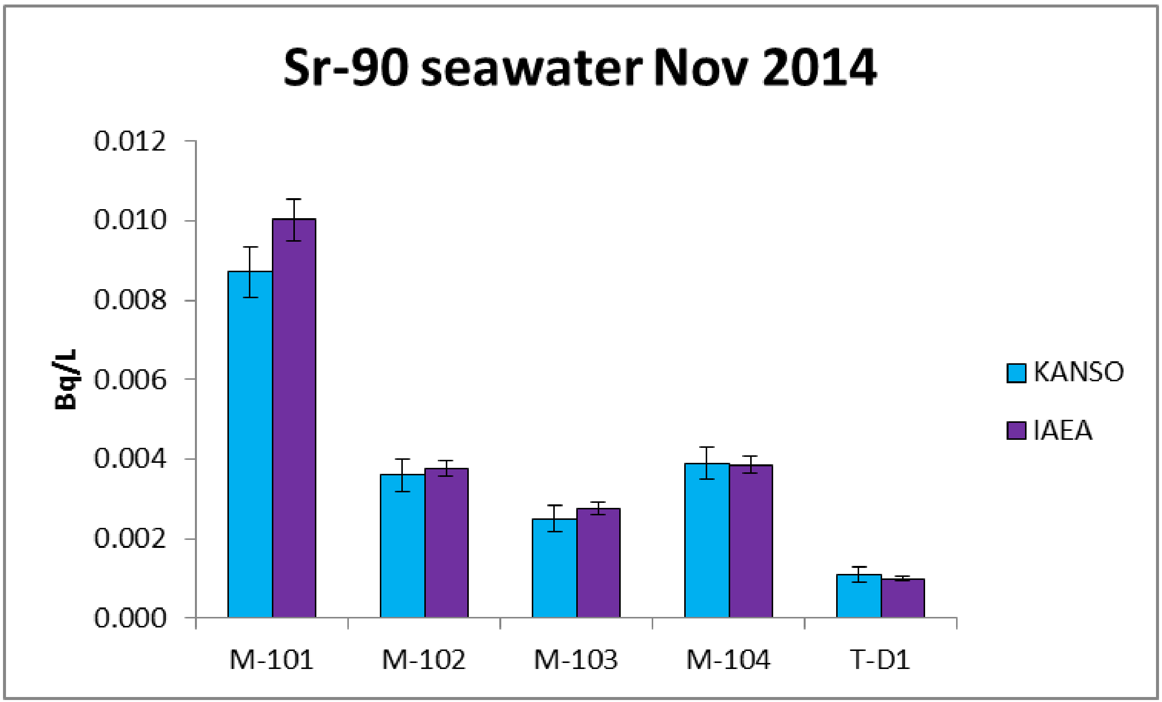

FIG. 7. Activity concentrations of ^{90}*Sr in seawater samples.*

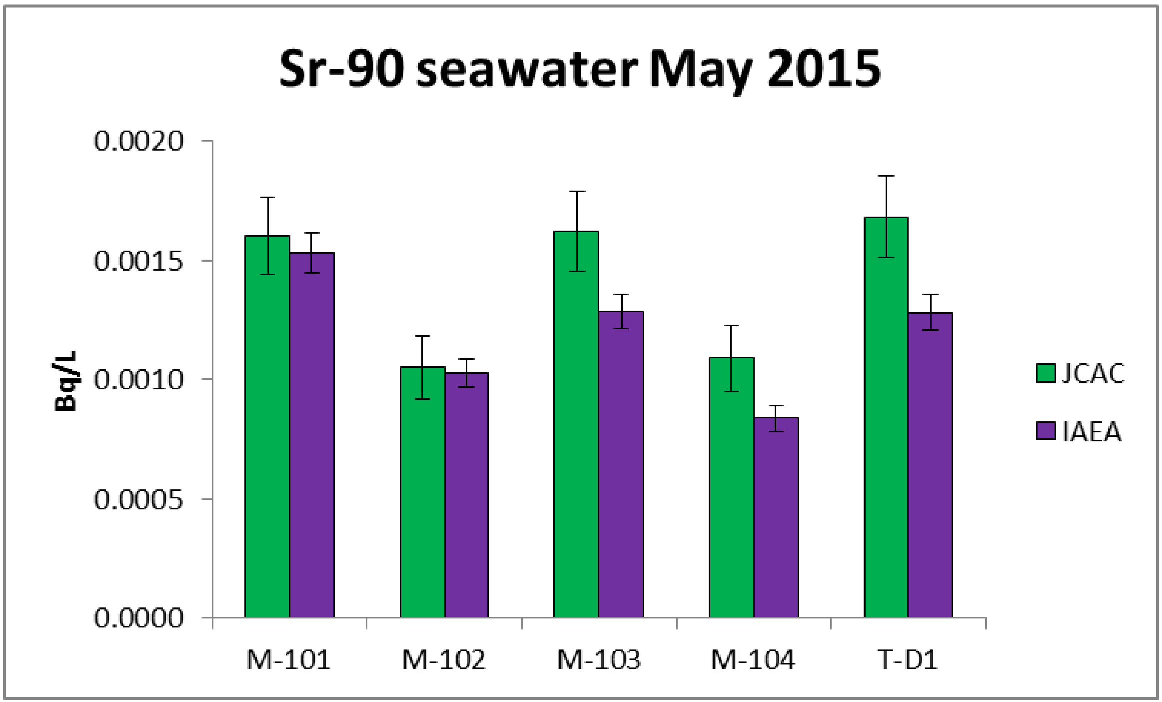

FIG. 8. Activity concentrations of ^{90}Sr in seawater samples.

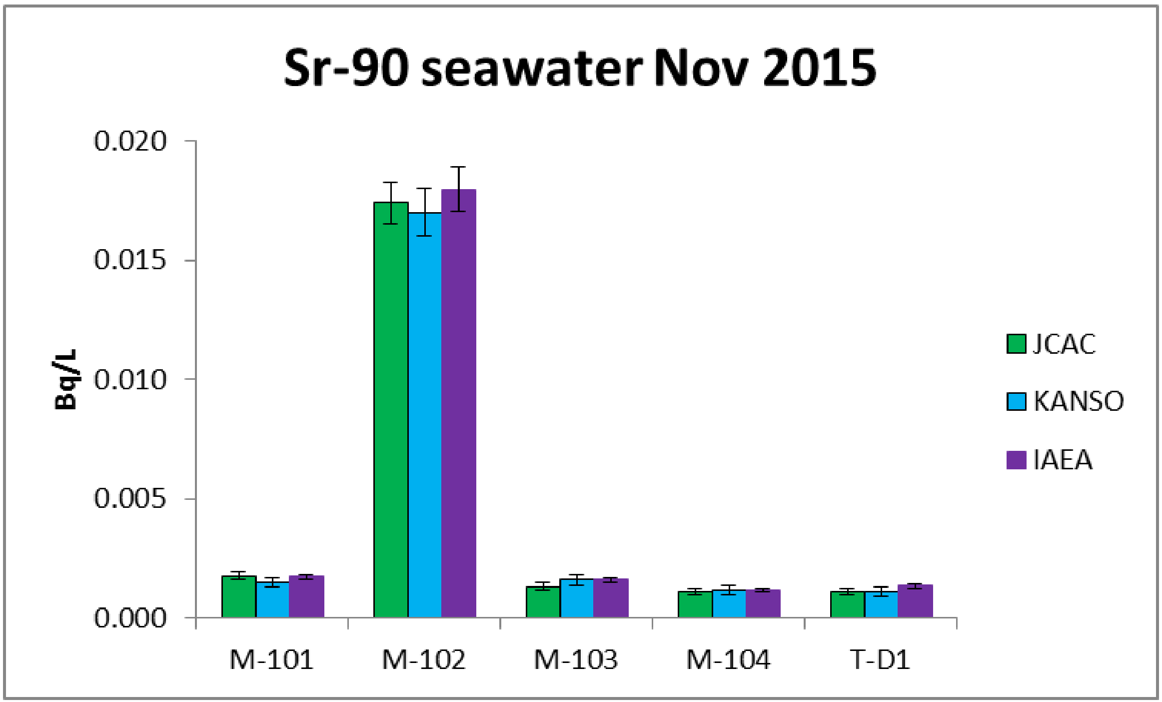

FIG. 9. Activity concentrations of ^{90}Sr in seawater samples.

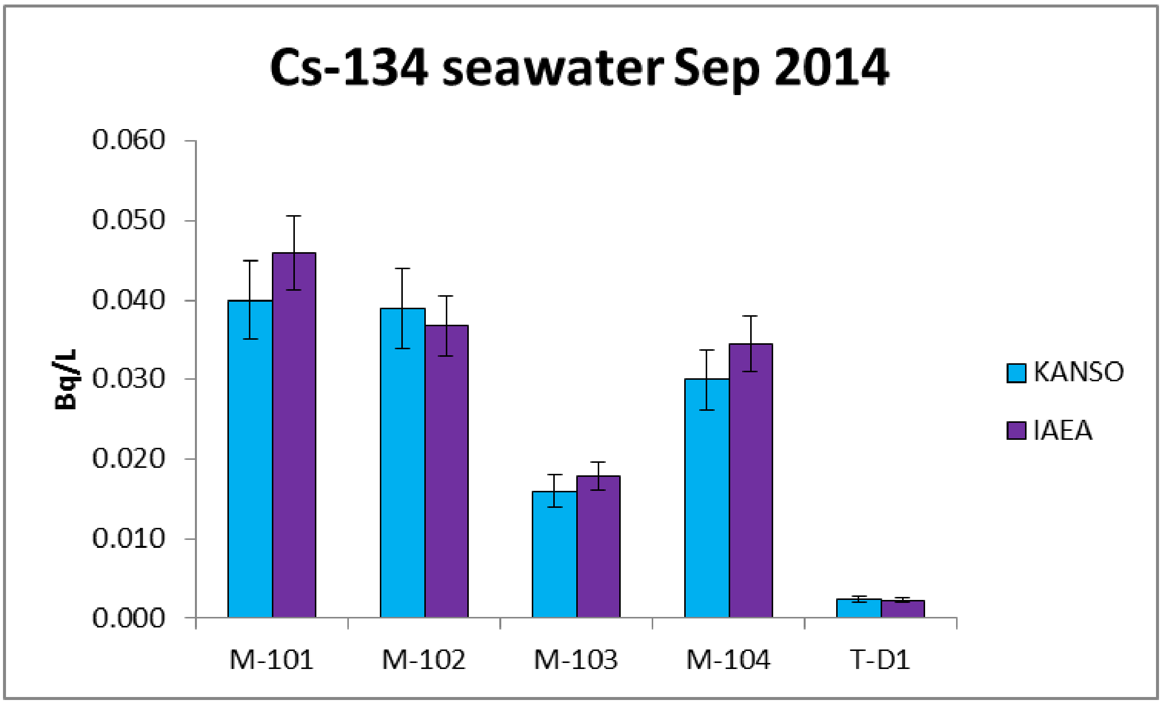

FIG. 10. Activity concentrations of ^{134}Cs in seawater samples.

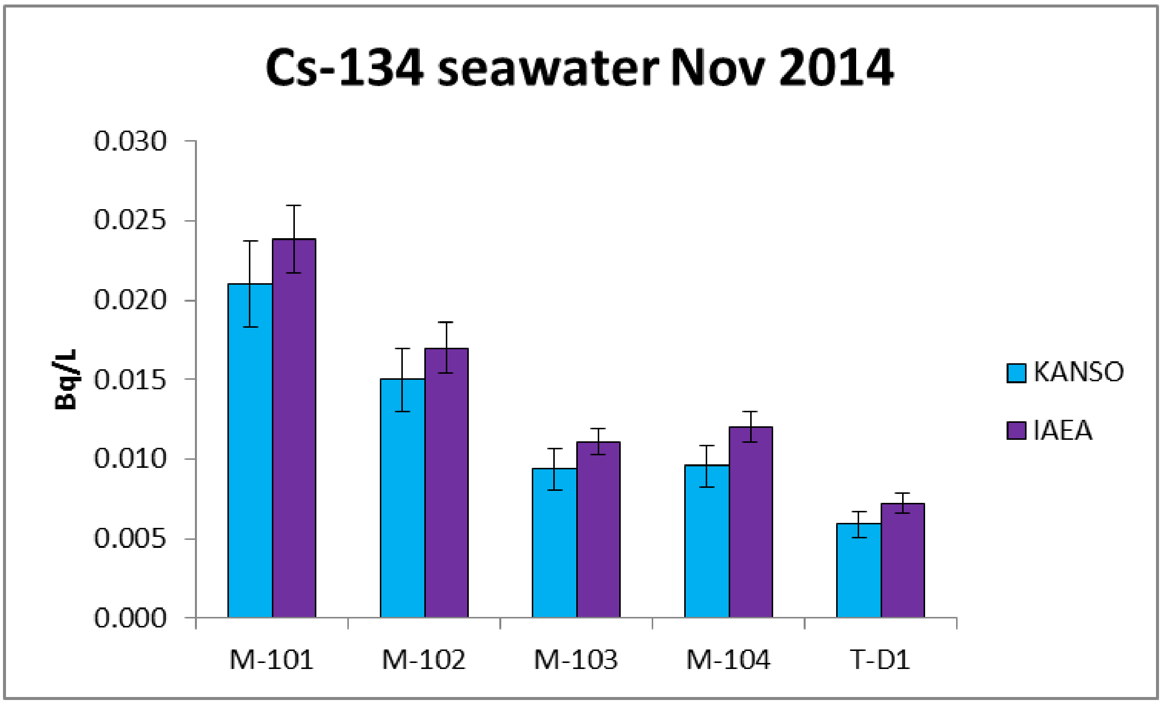

FIG. 11. Activity concentrations of ^{134}Cs in seawater samples.

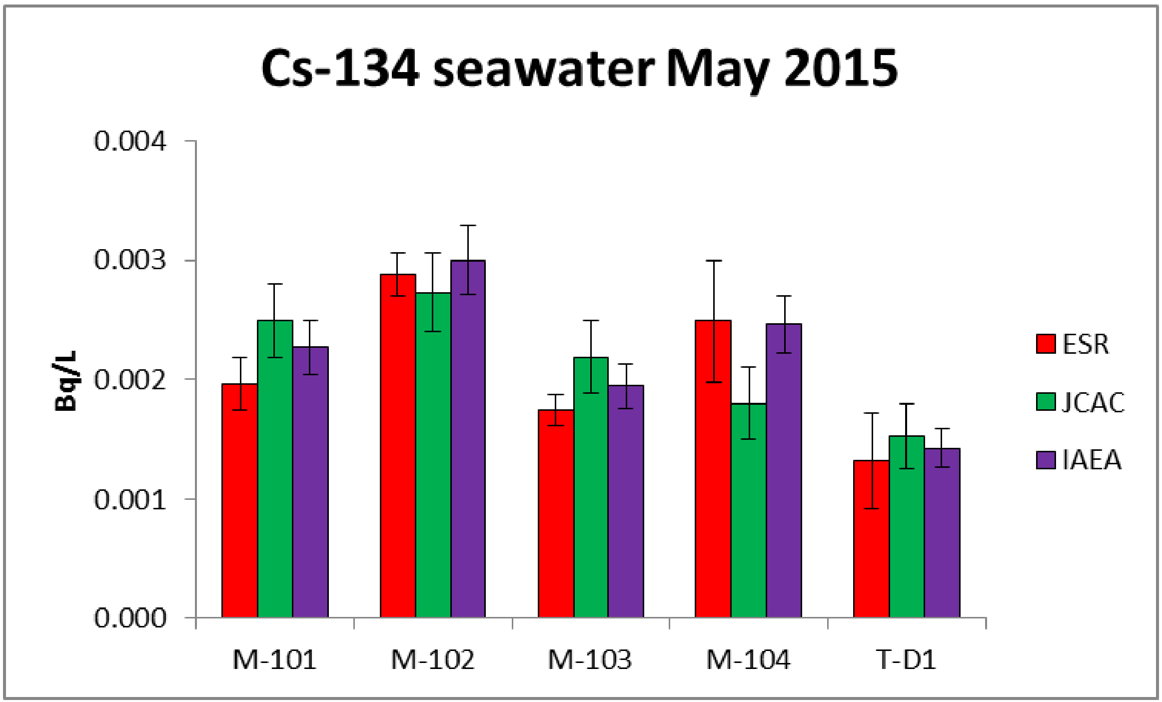

FIG. 12. Activity concentrations of ^{134}Cs in seawater samples.

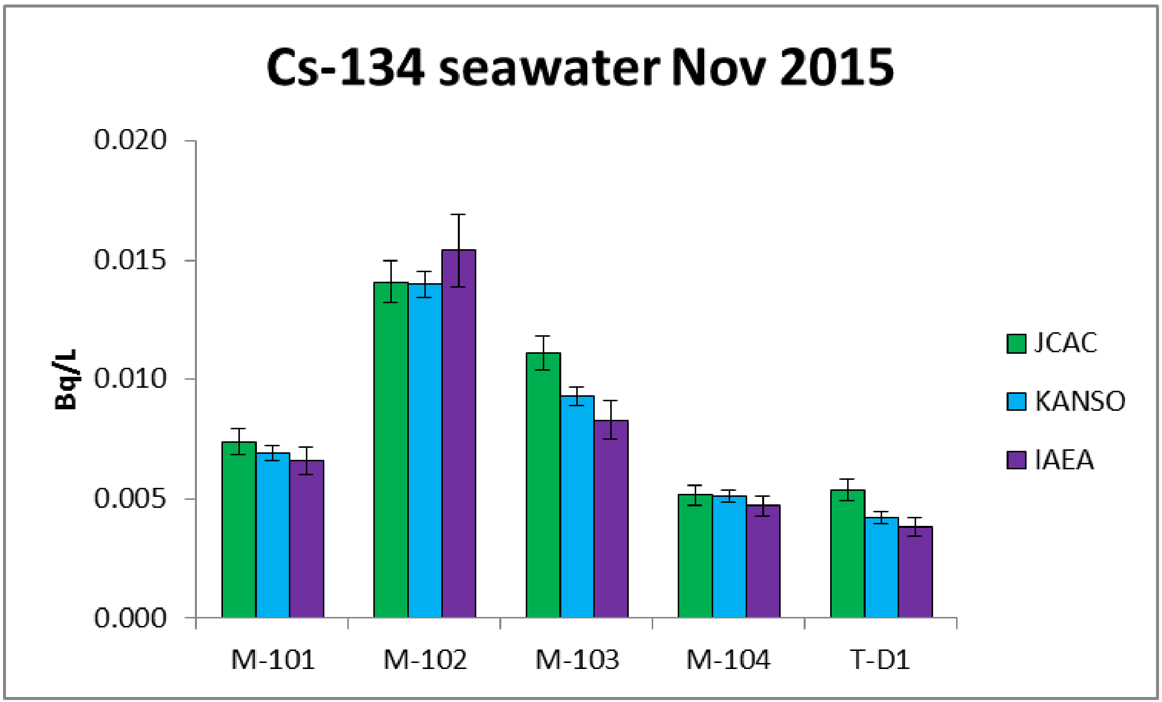

FIG. 13. Activity concentrations of ^{134}Cs in seawater samples.

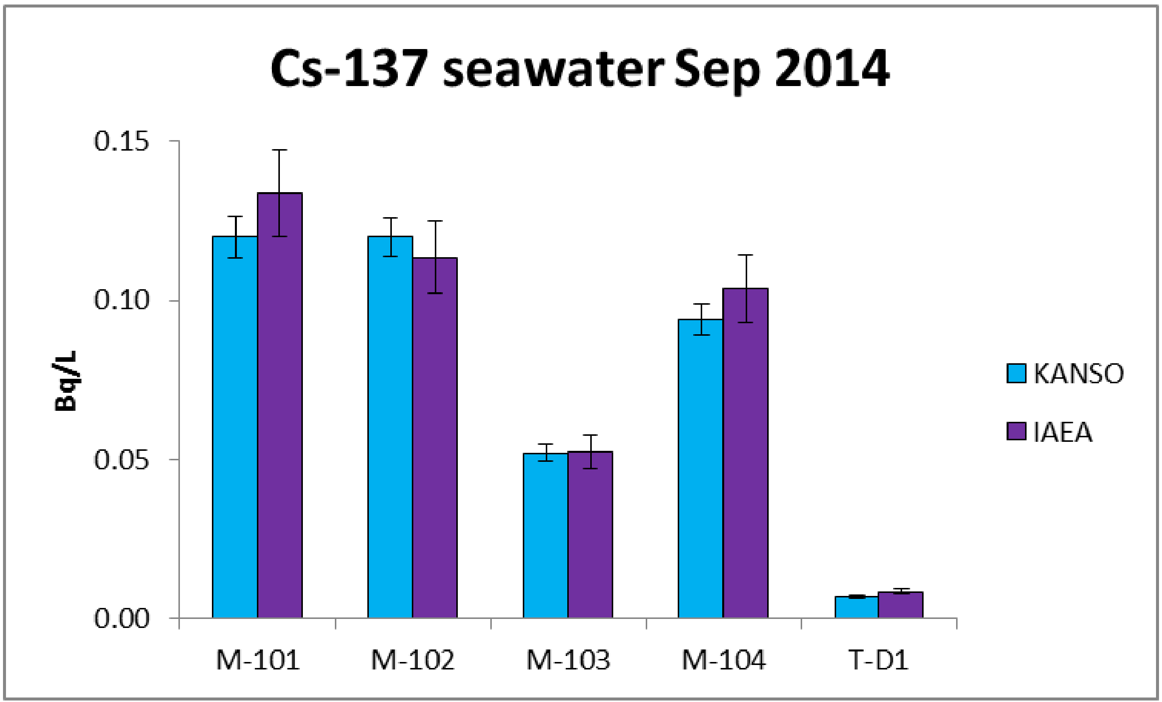

FIG. 14. Activity concentrations of ^{137}Cs in seawater samples.

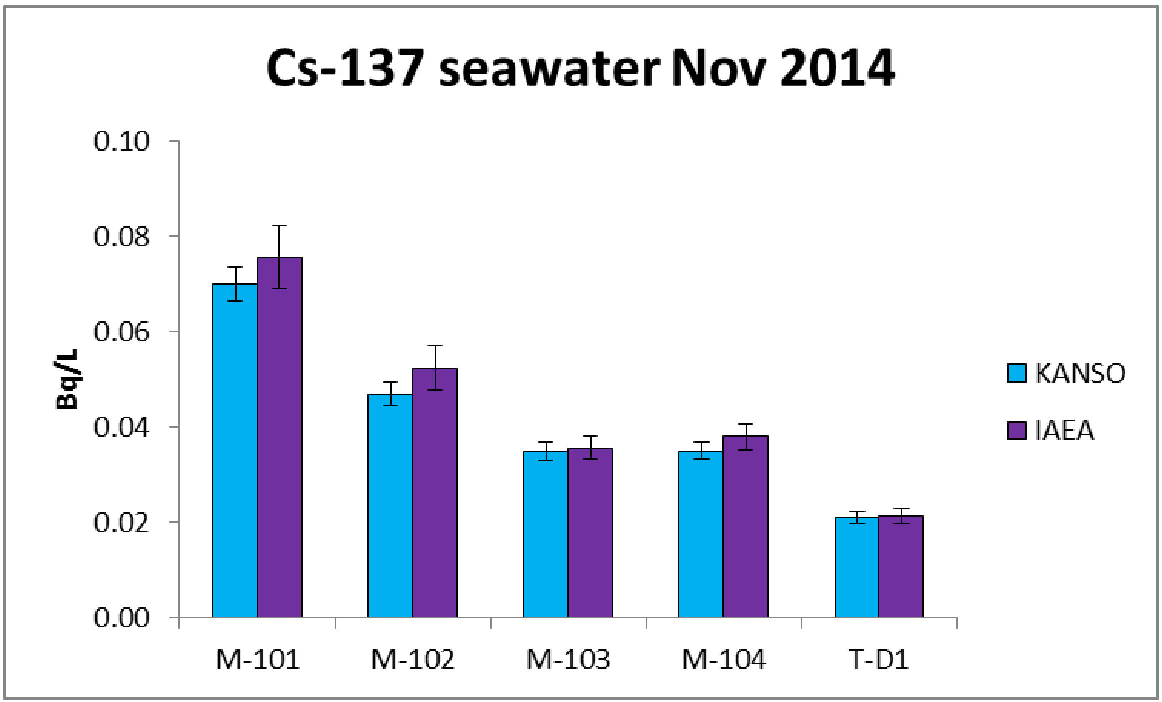

FIG. 15. Activity concentrations of ^{137}Cs in seawater samples.

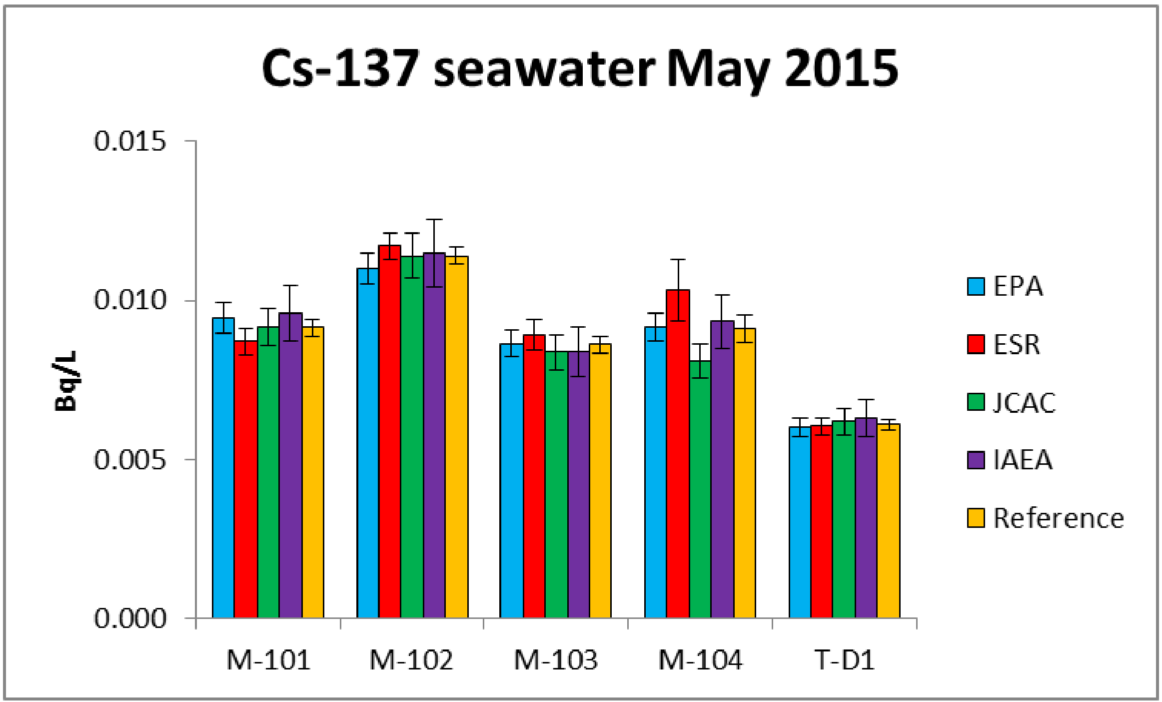

FIG. 16. Activity concentrations of ^{137}Cs in seawater samples.

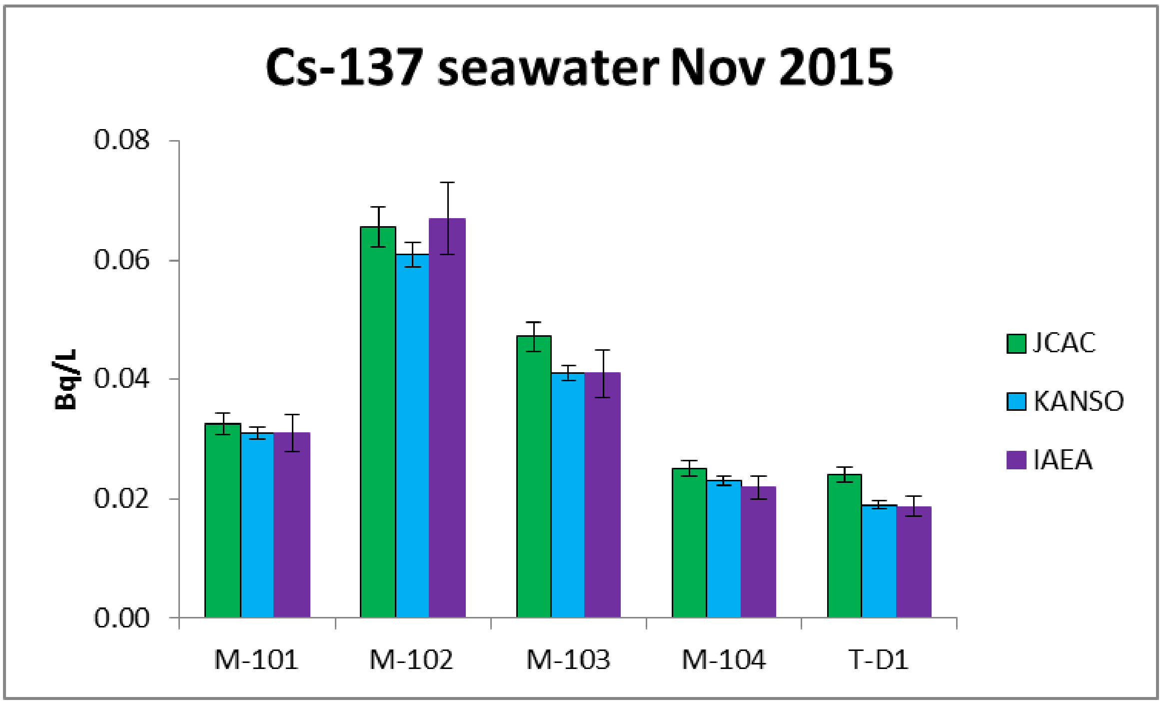

FIG. 17. Activity concentrations of ^{137}Cs in seawater samples.

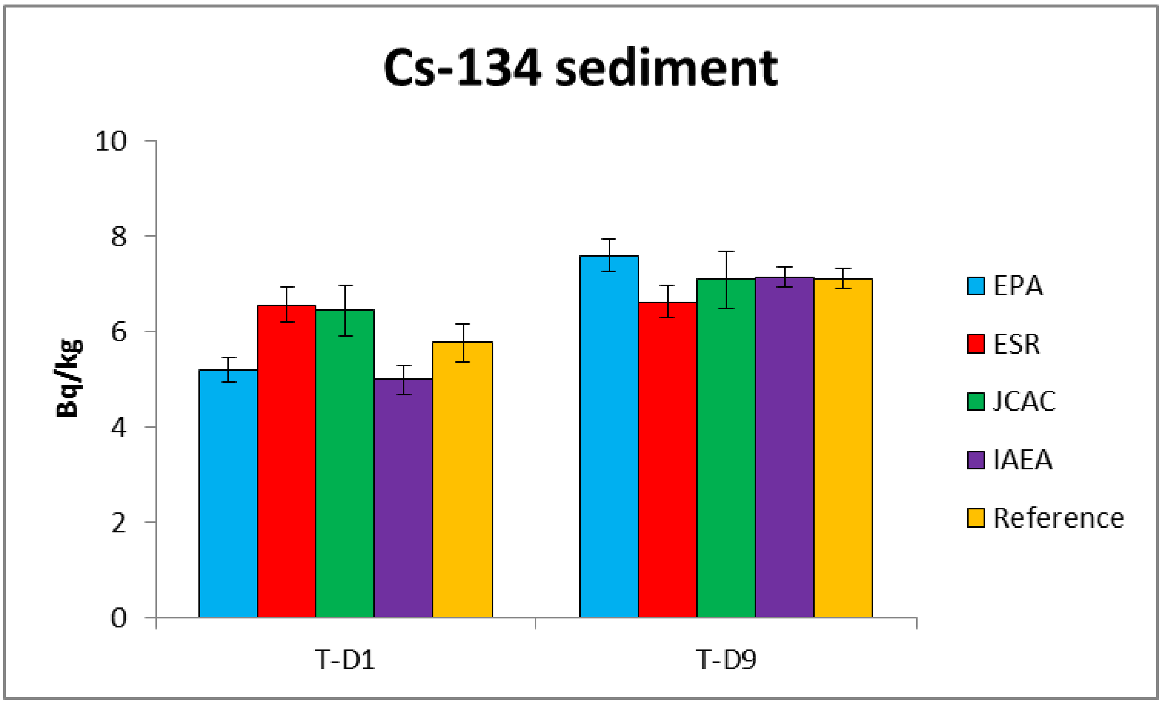

FIG. 18. Massic activities of ^{134}Cs in sediment samples.

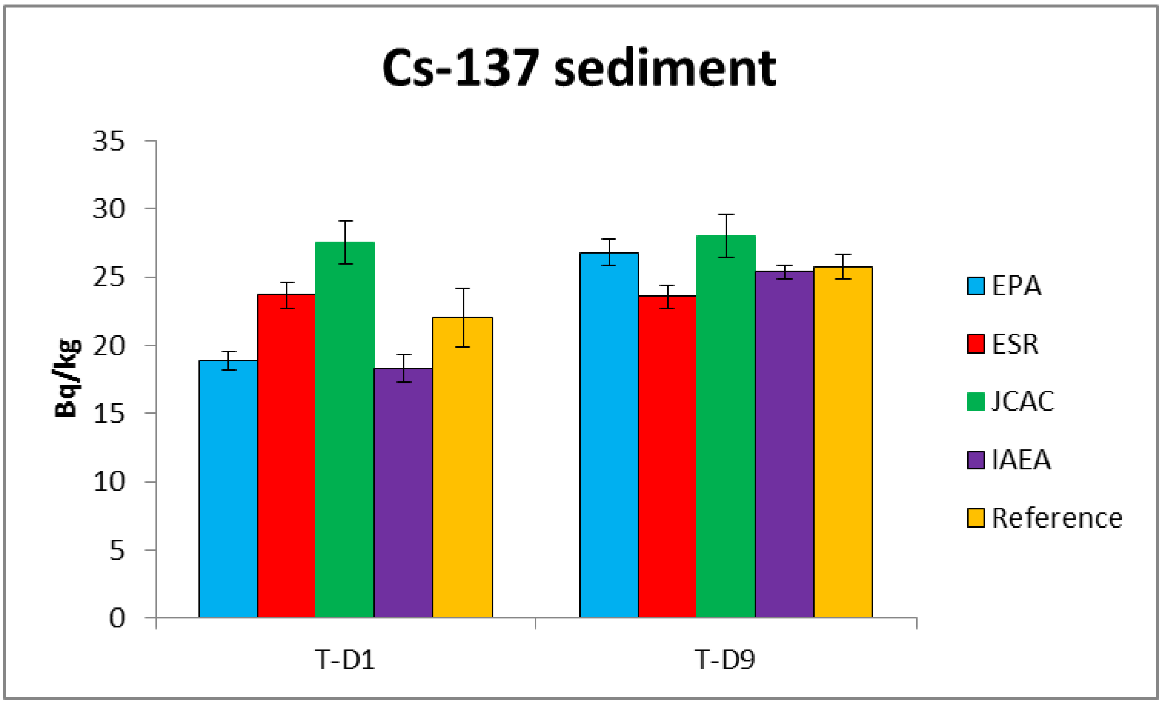

FIG. 19. Massic activities of ^{137}Cs in sediment samples.

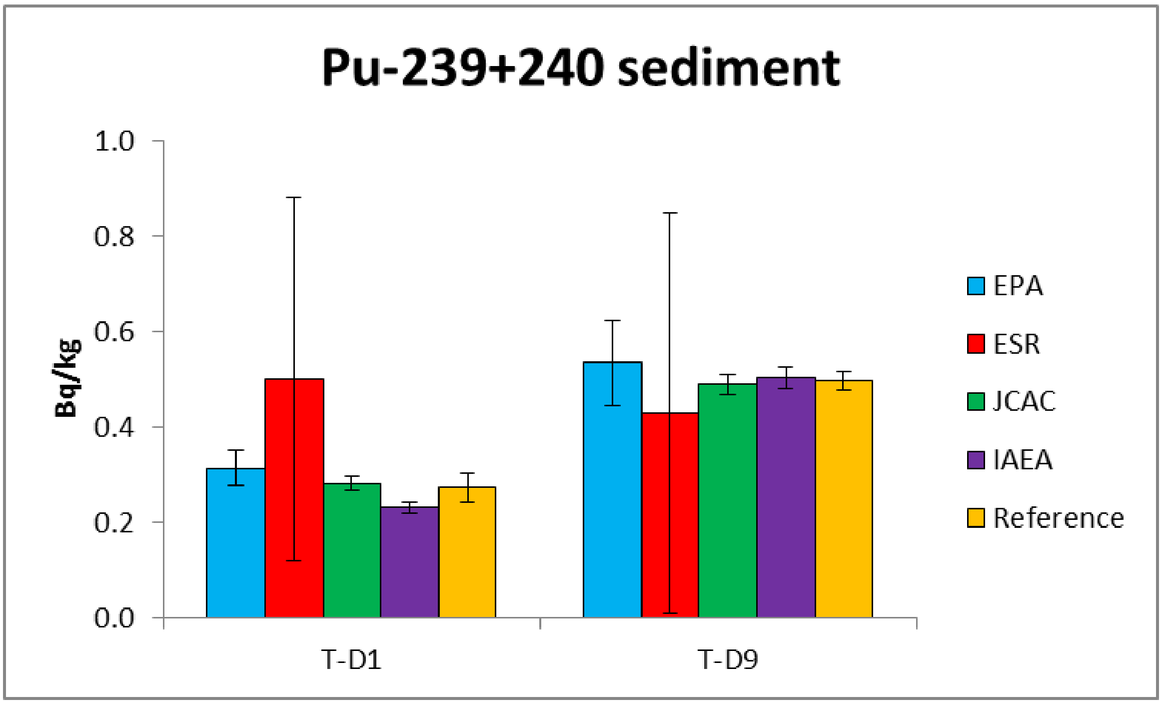

FIG. 20. Massic activities of $^{239+240}$*Pu in sediment samples.*

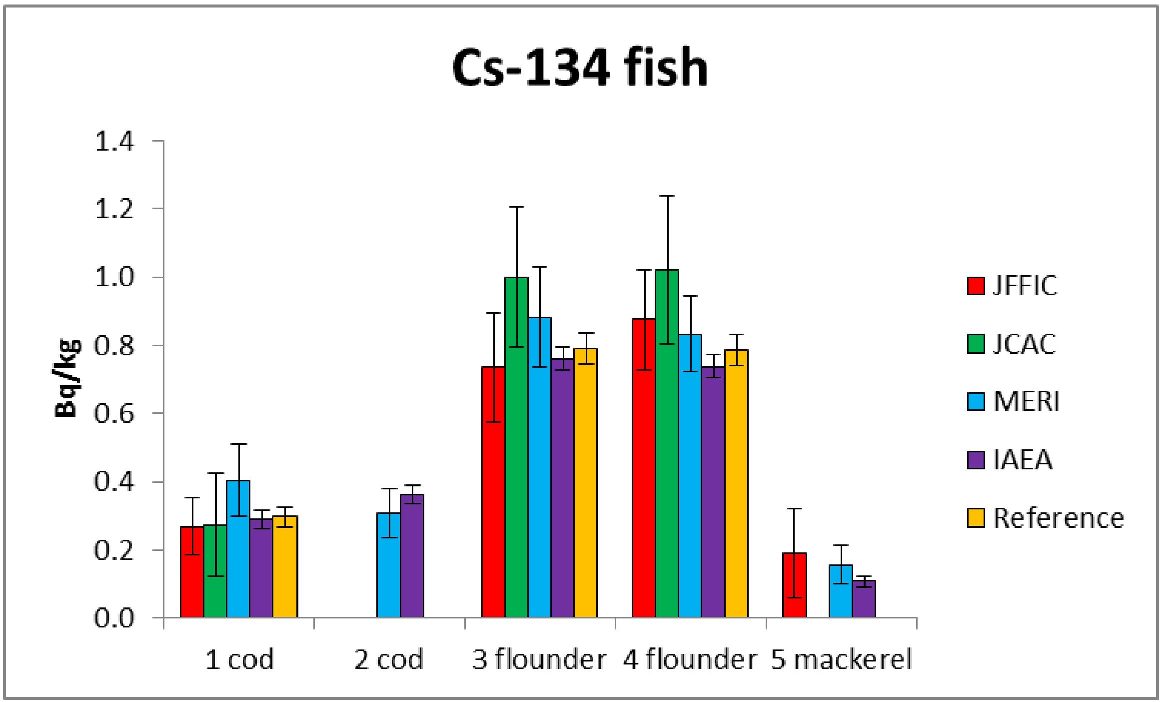

FIG. 21. Massic activities of ^{134}Cs in fish samples.

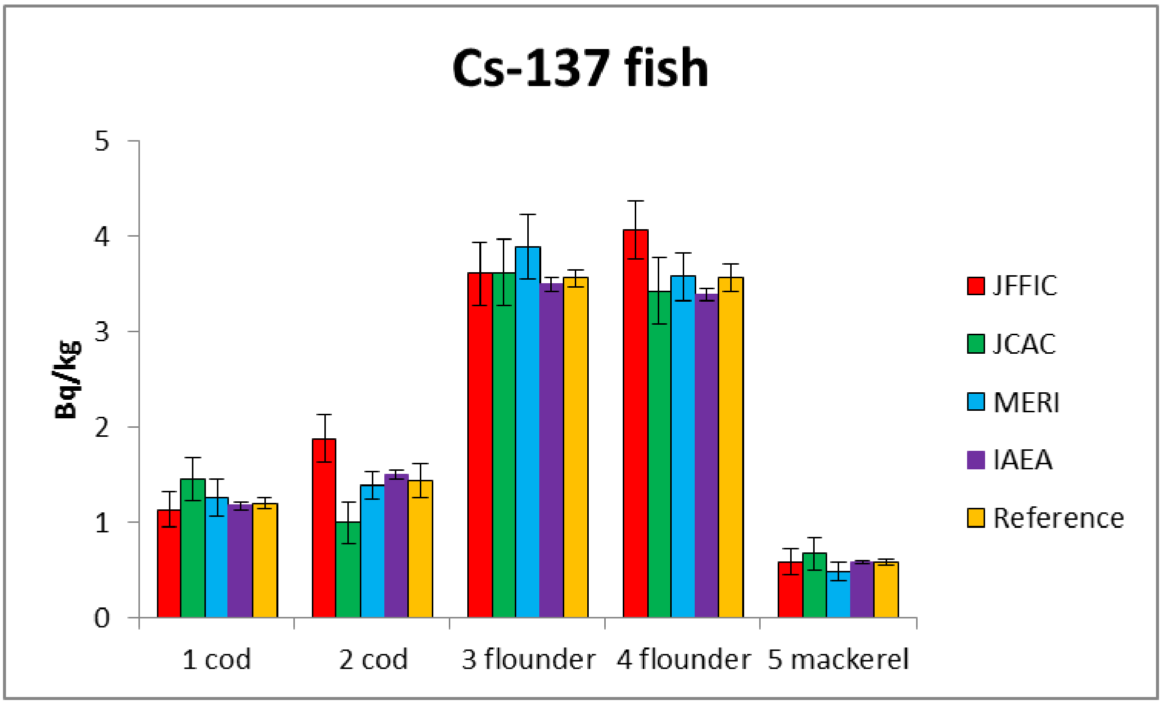

FIG. 22. Massic activities of ^{137}Cs in fish samples.